

binding complementary DNA to which the modulator **292** is bound to the DNA by hybridization and the like.

[0237] The method for binding the labeling substance **293** to the modulator **292** is performed by the same method as the method for binding the modulator **292** to the binding substance **291**.

[0238] Subsequently, the detection process is performed [see the detection process of FIG. 23D].

[0239] In the detection process, the user first injects an electrolytic solution through the sample inlet **30b** of the detection chip **20**. Thereafter, the user inserts the detection chip **20** into the chip insertion unit **11** of the detector **1** shown in FIG. 1. Then, the user gives an instruction to start measuring to the detector **1**. Here, the electrode leads **71**, **72**, and **73** of the detection chip **20** inserted into the detector **1** are connected to the ammeter **14** and the power source **15**. Then, an arbitrary potential based on the reference electrode **69** is applied to the working electrode body **61** by the power source **15** of the detector **1**. As the potential to be applied to the electrode, a potential in which the current value (stationary current, dark current) is low when the analyte is not irradiated with excitation light and the photocurrent generated from the analyte becomes a maximum photocurrent is preferred. The potential may be applied to the counter electrode **66** or the working electrode body **61**.

[0240] Thereafter, the light source **13** of the detector **1** emits excitation light to the labeling substance **293** on the working electrode **60**. Thus, the labeling substance **293** is excited to generate electrons. The generated electrons move to the working electrode **60**. As a result, current flows between the working electrode **60** and the counter electrode **66**. Then, the current flowing between the working electrode **60** and the counter electrode **66** is measured by the ammeter **14** of the detector **1**. The current value measured by the ammeter **14** correlates with the number of the labeling substance **293**. Therefore, the analyte S can be quantified based on the measured current value. The excitation light may be only light in a specified wavelength region, which is obtained using a spectrometer or a bandpass filter, if necessary.

[0241] Thereafter, a current value digitally converted by the A/D converting unit **16** is input into the control unit **17**. Then, the control unit **17** estimates the amount of the analyte in the sample from the digitally converted current value based on a calibration curve indicating a relationship between a current value created in advance and the amount of the analyte. The control unit **17** creates a detection result screen for displaying the information on the estimated amount of the analyte on the display **12**. Thereafter, the detection result screen created by the control unit **17** is sent to the display **12** so as to be displayed on the display **12**.

[0242] As the electrolytic solution, a solution containing an electrolyte composed of salts which may supply electrons to the labeling substance **293** in an oxidized state, an aprotic solvent or a protonic polar solvent can be used. The electrolytic solution may further contain other components, if desired. The electrolytic solution may be in gel or solid form.

[0243] As the electrolyte, the same electrolyte described in the first embodiment can be used.

[0244] The electrolyte concentration of the electrolytic solution is preferably from 0.001 to 15 M.

[0245] When the labeling substance **293** is irradiated with light, a light source which can emit light in a wavelength capable of photoexciting the labeling substance **293** can be used. The light source can be suitably selected depending on

the type of the labeling substance **293**. As the light source, the same light source described in the first embodiment can be used.

[0246] In the measurement of a photocurrent derived from the labeling substance **293**, for example, a measurement device which includes an ammeter, a potentiostat, a recorder, and a computer can be used.

[0247] In the detection process, the amount of the analyte can be examined by quantifying the photocurrent.

[0248] As described above, in the method for electrochemically detecting an analyte according to the present embodiment, when detecting the analyte S, the modulator **292** intervenes between the binding substance **291** and the labeling substance **293** [see FIG. 23D]. On the other hand, in the conventional method for electrochemically detecting an analyte, for example, as shown in FIG. 24A, a labeled antibody **201** obtained by directly labeling an antibody **202** as a binding substance with a labeling substance **203** is used in labeling of the analyte S. A complex containing the trapping substance **281** on the working electrode body **61**, the analyte S, and the labeled antibody **201** is formed, and the analyte S is detected based on the current (photocurrent) generated from the labeling substance **203** in the complex formed on the electrode. Thus, in the conventional method shown in FIG. 24, the specific volume of the complex formed in detecting the analyte S becomes a large restriction in achieving high sensitivity. Thus, the photocurrent being detected tends to be small.

[0249] However, in the method for electrochemically detecting an analyte according to the second embodiment of the present invention, the specific volume of the complex to be formed on the working electrode **60** is larger than that of the complex formed when labeling the analyte S by the conventional method shown in FIG. 24. Despite that, the analyte can be unexpectedly detected with high detection sensitivity as compared with the conventional method shown in FIG. 24.

[0250] In the method for electrochemically detecting an analyte according to the present embodiment, from the viewpoint of suppressing the generation of noises due to contaminants, the user may discharge a remaining liquid containing contaminants from the sample inlet **30b** of the detection chip **20** after the process of trapping an analyte and wash an inside of the detection chip **20**. In the washing of the inside of the detection chip **20**, organic solvents such as a buffer (particularly a buffer containing a surfactant); purified water (particularly purified water containing a surfactant); and ethanol can be used.

[0251] In the method for electrochemically detecting an analyte according to the present embodiment, from the viewpoint of removing free label binding substance **290** which is not bound to the analyte S and improving the detection accuracy, the process of washing the inside of the detection chip **20** to remove the free label binding substance **290** may be further performed after the labeling process. For example, ethanol and purified water can be used for the washing.

[0252] In the present invention, the operation may be performed so as to form a label binding substance in the labeling process as shown in FIG. 25 in place of labeling the analyte S using the label binding substance to which the labeling substance is bound in advance in the labeling process. In the method for electrochemically detecting an analyte shown in FIG. 25, the process of supplying a sample (FIG. 25A), the process of trapping an analyte (FIG. 25B), and the detection process (FIG. 25D) are the same as the process of supplying a sample (FIG. 23A), the process of trapping an analyte (FIG.